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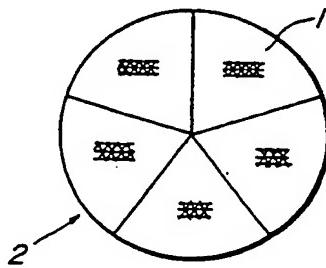
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(54) Ceramic heat exchangers and production thereof.

(57) A ceramic heat transmission type or regenerative heat exchanger (2) comprises a plurality of matrix segments (1) bonded together with a bonding material. Difference in coefficient of thermal expansion between the matrix segments (1) and the bonding material is not more than 0.02% at 800 °C, and a Young's modulus of the bonding material is not less than 0.4 time to not more than 1.8 times that of the matrix segment (1). A process for producing ceramic heat exchangers (2) comprises the steps of extruding and firing honeycomb structural segments in which a crystalline phase is mainly composed of cordierite and a coefficient of thermal expansion in an extending direction of flow channels is not more than 0.06% at 800 °C, machining an outer periphery of each of the segments (1), coating the bonding material around the outer periphery of each of the segments (1), bonding the segments (1) together, and drying and firing the bonded segments (1).

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FIG. 1



CERAMIC HEAT EXCHANGERS AND PRODUCTION THEREOF

The present invention relates to ceramic heat exchangers having excellent heat exchange efficiency, small pressure loss and excellent thermal shock resistance, and the invention also relates to a production process thereof.

As rotary regenerative ceramic heat exchangers having excellent thermal shock resistance, NGK Insulators, Ltd. formerly discloses a process capable of producing heat exchangers in Japanese patent publication No. 61-51,240 (U.S. Patent 4,304,585 and U.S. Patent 4,357,987), wherein matrix segments are bonded together with a ceramic-bonding material having almost the same composition as that of the matrix segments and a difference in coefficient of thermal expansion between the bonding material and the segments is not more than 0.1% at 800 °C.

Further, Japanese patent publication No. 47-14,838 (U.S. Patent 3,634,111) discloses a foamable cement consisting mainly of Li_2O , Al_2O_3 , SiO_2 , and TiO_2 as an example of the ceramic-bonding material. In addition, U.S. Patent No. 4,335,783 discloses a process for producing heat exchangers in which bonded portions are discontinuous.

On the other hand, in the case of Japanese patent publication No. 61-51,240 (U.S. Patent 4,304,585 and U.S. Patent 4,357,987), heat exchanger having considerably excellent thermal shock resistance can be obtained. However, since the rotary regenerative heat exchanger requires high thermal shock resistance, the matrix segments themselves must exhibit low thermal expansion, and it is also necessary to employ the bonding material exhibiting low thermal expansion, such heat exchangers possess problems in that the bonding material exhibiting low thermal expansion is greatly shrank during firing, that variations in bonding strength is great, and that reliability of the bonded portion is deteriorated.

In the case of the foamable cement disclosed in Japanese Patent publication No. 47-14,838 (U.S. Patent 3,634,111), bonding materials exhibiting low heat expansion and small shrinkage can be obtained. However, when cordierite matrixes are bonded by using this foamable cement, the foamable cement is insufficiently crystallized during firing for the bonding. That is, the cement reacts with cordierite, so that the coefficient of thermal expansion of the bonded portions increases, and that a dimensional change and a change in heat expansion during isothermal aging at high temperatures are great. Consequently, the ceramic matrix product will unfavorably be broken from the joined portions during practical use.

In the case of the discontinuous bonding process described in U.S. Patent No. 4,335,783, the entire heat exchanger is designed to have a flexible structure and to lessen difference in temperature between the bending material and the segments by discontinuous bonding so that propagation of cracks is prevented to improve thermal shock resistance. However, strength of the partially bonded portions is unfavorably poorer than that of the entire bonded product in the case of the great size bonded product.

It is an object of the present invention to solve the above-mentioned problems, and to provide ceramic heat exchangers having excellent heat exchange efficiency, small pressure loss, and excellent thermal shock resistance. The invention is also to provide a process for producing such ceramic heat exchangers.

The ceramic heat exchangers according to the present invention are ceramic heat transmission type heat exchangers or regenerative heat exchangers, characterized in that difference in coefficient of thermal expansion between matrix segments and a bonding material is not more than 0.02% at 800 °C, and that a Young's modulus of the bonding material is not less than 0.4 time to not more than 1.8 times that of the matrix segments.

The process for producing ceramic heat exchangers according to the present invention is characterized by comprising the steps of extruding and firing honeycomb structural matrix segments in which a main component of a crystalline phase is cordierite and which have a coefficient of thermal expansion in a direction of flowing channels being not more than 0.06% at 800 °C, machining the outer peripheries thereof, coating a bonding material on the outer peripheries, and bonding the matrix segments, which are dried and fired, the bonding material having a thermal expansion different from that of the matrix segments by not more than 0.02% at 800 °C after the firing, a Young's modulus of the bonding material being not less than 0.4 time to not more than 1.8 times that of the matrix.

In the above construction, the matrix segments which has the coefficient of thermal expansion of not more than 0.06% at 800 °C in a flowing direction and the bonding material which has the specified difference in coefficient of thermal expansion between the matrix segments and the bonding material, and which has the specified Young's modulus are used. Thereby, stress concentration upon the bonded portions is prevented so that the ceramic heat exchanger having excellent thermal shock resistance can be obtained. The present invention is based on the above-mentioned novel discovery.

These and other optional features and advantages of the invention will be appreciated upon reading of

the following description of the invention when taken in conjunction with the attached drawings, with the understanding that some modifications, variations and changes of the same could be made by the skilled person in the art to which the invention pertains.

For a better understanding of the invention, reference is made to the attached drawings, wherein:

5 Figs. 1 through 3 are views of embodiments of the ceramic heat exchangers according to the present invention.

First, the limitations made in the present invention will be explained below.

The reason why the difference in coefficient of thermal expansion between the matrix segment and the bonding material is set at not more than 0.02% at 800°C is that if it exceeds 0.02%, thermal shock resistance of the bonded portions will not meet the range aimed at in the invention. On the other hand, the reason why the Young's modulus of the joined portions is limited to not less than 0.4 time to not more than 1.8 times that of the matrix segment is that if it is less than 0.4 time, strength of the bonded body itself is far weaker than that of the matrix, while if it exceeds 1.8 times, the thermal shock resistance of the bonded portions does not meet the intended range in the present invention.

15 In the case of LAS glass, the intended coefficient of thermal expansion of the bonding material can be attained by adjusting the composition to 55.0 to 78.0% by weight of SiO₂, 12.0 to 25.0% by weight of Al₂O₃, not more than 0.2% by weight of each of Na₂O and K₂O, 1.0 to 3.0% by weight of CaO, and 3.0 to 6.0% by weight of Li₂O. The Young's modulus of the bonding material can appropriately be adjusted by adding into the bonding material a given amount of a foaming agent which forms pores after firing, such as 20 graphite, carbon powder or resin beads. Any one of the above-mentioned processes is a favorable process for attaining the coefficient of thermal expansion and the Young's modulus as desired. It goes without saying that so long as the coefficient of thermal expansion and the Young's modulus of the bonding material can be obtained as desired, any process may be employed.

In order to obtain rotary regenerative ceramic heat exchangers by the producing process according to 25 the present invention, a green body is extruded in the form of a honeycomb structural matrix segment having a triangular, rectangular, or hexagonal cell shape or the like, which is then fired. Thereafter, as shown in Figs. 1 through 3 by way of example, a plurality of such segments 1 in which as main component of a cordierite has a coefficient of thermal expansion of not more than 0.06% at 800°C are machined to produce an integrated rotary regenerative ceramic heat exchanger 2 therefrom, coating a ceramic bonding 30 material as an LAS based amorphous glass powder having a chemical composition consisting mainly of Li₂O, Al₂O₃, and SiO₂ upon the segments in such a thickness to be 0.1 to 6 mm after firing, fully drying, and then firing at 1,100 to 1,200°C for 1 to 4 hours. Thereby, the rotary regenerative ceramic heat exchanger can be obtained.

It is possible that the difference in coefficient of thermal expansion between the matrix segments and 35 the bonding material and the Young's modulus of the bonding material are adjusted to not more than 0.02% at 800°C and 0.4 time to 1.8 times that of the matrix, respectively, by adjusting the composition of the bonding material, such as Li₂O, Al₂O₃, and SiO₂ and adding the foaming agent thereto.

Now, actual examples of the present invention will be explained.

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Examples

By extruding a green body, segments A with cells each having a long side of 1.2 mm and a short side of 0.8 mm and segments B with cells having a long side of 1.0 mm and a short side of 0.5 mm were shaped. The wall thickness of the segments was 0.1 mm. Then, two kinds of matrix segments of 130 × 180 × 170 mm were prepared by firing the above segments at 1,400°C for 6 hours. At that time, 35 × 6 of the matrix segments were obtained for each kind. The outer periphery of each of these two kinds of the segments was machined to give an integral rotary regenerative heat exchanger after bonding. Next, a pasty bonding material was applied to portions of the segments to be bonded in such a thickness that the 50 thickness of the bonding material after the firing might be 1.5 mm. Then, the segments were bonded, which were fully dried and fired at 1,150°C for 2 hours. The above pasty bonding material was obtained by adding 2.0, 5.0, 10.0, 20.0 or 30.0% by weight of graphite as a foaming agent to an LAS based amorphous glass powder having a chemical composition of 70.0% by weight of SiO₂, 24.0% by weight of Al₂O₃, 4.3% by weight of Li₂O, and 1.5% by weight of CaO, and further adding an organic binder and water thereto. 55 Thereby, an integrated rotary regenerative heat exchanger having a diameter of 700 mm and a thickness of 70 mm was obtained. Furthermore, for the comparison purpose, a conventional rotary regenerative heat exchanger was prepared in the same manner as mentioned above by using a bonding material to which no foaming agent was added.

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A fired sample of the bonding material was obtained by drying the above bonding material and firing it under the same conditions mentioned above, and used for measuring the Young's modulus. A thermal shock resistance-evaluating test and a fracture-evaluating test were carried out for an integral structure and at a bonded portion, respectively. Results are shown in Table 1. The thermal shock resistance was evaluated based on the maximum temperature at which the sample was not cracked even when extracted from an electric furnace after having been held in a specific location of the furnace. Fracture test was determined by preparing a sample having 4 × 3 × 40 mm in which a bonded portion was located at the center, and effecting a four point bending test. Further, the Young's modulus of the matrix was measured in such a direction that long sides of the cells were arranged parallel with the longitudinal direction of the sample. A loading direction was parallel with the cell channels.

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Table 1

Run No.	Bonding material			Matrix			Ratio in Young's modulus	Broken position	Thermal shock-resisting temperature (°C)	Remarks
	Added amount of graphite (wt%)	Coefficient of thermal expansion (%)	Young's modulus ($\times 10^2$ kg/mm 2)	Cell structure ³⁾	Coefficient of thermal expansion ²⁾ (%)	Young's modulus ¹⁾ ($\times 10^2$ kg/mm 2)				
1	0	0.034	12.5	Ⓐ	0.060	3.5	0.026	3.6 segment	600	Reference Example
2				Ⓑ	0.050	5.0	0.016	2.5 "	650	"
3	2.0	0.036	9.0	Ⓐ	0.060	3.5	0.024	2.6 "	700	"
4				Ⓑ	0.050	5.0	0.014	1.8 "	750	Present invention
5	5.0	0.038	6.3	Ⓐ	0.060	3.5	0.022	1.8 "	700	Reference Example
6				Ⓑ	0.050	5.0	0.012	1.3 "	800	Present invention
7	10.0	0.040	3.6	Ⓐ	0.060	3.5	0.020	1.0 "	800	"
8				Ⓑ	0.050	5.0	0.010	0.7 "	850	"
9	20.0	0.042	2.0	Ⓐ	0.060	3.5	0.018	0.6 "	750	"
10				Ⓑ	0.050	5.0	0.008	0.4 "	800	"
11	30.0	0.045	1.4	Ⓐ	0.060	3.5	0.015	0.4 "	750	"
12				Ⓑ	0.050	5.0	0.005	0.3 bonded portion broken	700	Reference Example

¹⁾ measured by Miller process²⁾ 40-800 °C³⁾ Ⓐ: 1.2 mm × 0.8 mm, Ⓑ: 1.0 mm × 0.5 mm

From the above results, it is seen that as compared with Reference Example Nos. 1 through 3, 5 and
12. Examples 4 and 6 through 11 according to the present invention using the bonding material with the
difference in coefficient of thermal expansion and the ratio in Young's modulus as specified have higher
5 thermal shock resisting temperatures and are free from fracture from the bonded portions.
As is clear from the above-mentioned explanation, according to the ceramic heat exchanger and the
production process thereof in the present invention, the ceramic heat exchangers having excellent thermal
shock resistance can be obtained by using the bonding material suited for the properties of the matrix

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Claims

1. A ceramic heat transmission type or regenerative heat exchanger comprising a plurality of matrix segments, said matrix segments being bonded together with a bonding material, wherein a difference in coefficient of thermal expansion between the matrix segments and the bonding material is not more than 0.02% at 800°C and a Young's modulus of the bonding material is not less than 0.4 time to not more than 1.8 times that of the matrix segments.
2. A process for producing ceramic heat exchangers, said process comprising the steps of extruding cordierite and a coefficient of thermal expansion in an extending direction of flow channels is not more than 0.06% until 800°C, machining an outer periphery of each of the segments, coating a bonding material around the outer periphery of each of the segments, bonding the segments together, and drying and firing the bonded segments. The bonding material having a coefficient of thermal expansion different from that of the matrix segments after the firing by not more than 0.02% at 800°C, and a Young's modulus of the bonding material being not less than 0.4 time to not more than 1.8 times that of the matrix.

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FIG. 1

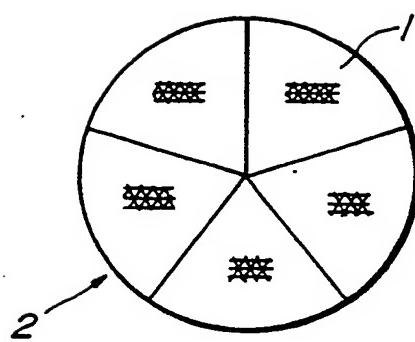


FIG. 2

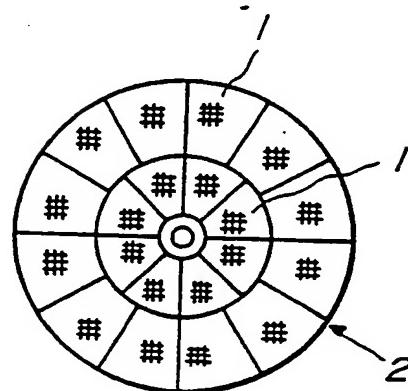
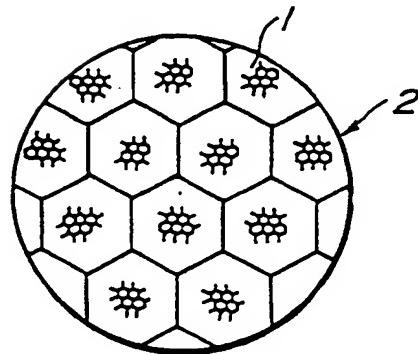


FIG. 3





EUROPEAN SEARCH REPORT

EP 89 30 9815

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D, A	US-A-4 357 987 (ODA et al.) * Column 4, lines 64-67; claims 1,2; figures * ---	1,2	F 28 D 19/04 F 28 F 21/04 C 04 B 37/00
D, A	US-A-4 304 585 (ODA et al.) * Column 4, lines 55-58; claim 1; figures * ---	1,2	
A	US-A-4 381 815 (FROST et al.) * Abstract; column 2, lines 39-62; column 6, lines 23-32; figure 2 * ---	1,2	
A	EP-A-0 082 608 (NGK) * Page 11, lines 17-20; claim 1 *	1,2	
A	EP-A-0 115 120 (NGK) * Abstract; figure 2 *	1,2	
A	DE-A-3 219 158 (DORNIER SYSTEM) * Page 4, lines 6-27 *	1,2	
A	US-A-4 595 662 (MOCHIDA et al.) -----		TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			F 28 F F 28 D C 04 B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	12-12-1989	HOERNELL, L.H.
CATEGORY OF CITED DOCUMENTS		
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document		